PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 01 March 2001 (01.03.01)	
International application No. PCT/EP00/06203	Applicant's or agent's file reference 10643q
International filing date (day/month/year) 03 July 2000 (03.07.00)	Priority date (day/month/year) 01 July 1999 (01.07.99)
Applicant BAUER, Monika et al	

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International Preliminary Examining Authority on:

   16 January 2001 (16.01.01)

   [ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer F. Baechler Telephone No.: (41-22) 338.83.38

Form PCT/IB/331 (July 1992)

EP0006203

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
PCFHG01		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 00/ 06203	03/07/2000	01/07/1999
Applicant		
PIRELLI CAVI E SISTEMI S.p.A.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 02 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

[ ] contained in the international application in written form.
[ ] filed together with the international application in computer readable form.
[ ] furnished subsequently to this Authority in written form.
[ ] furnished subsequently to this Authority in computer readble form.
[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

[X] the text is approved as submitted by the applicant.
[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

[X] the text is approved as submitted by the applicant.
[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ---

[ ] as suggested by the applicant.
[ ] because the applicant failed to suggest a figure.
[ ] because this figure better characterizes the invention.

[X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/06203

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G73/06 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 780 159 A (BAUER MONIKA ET AL) ? [illegible] see declaration 14 July 1998 (1998-07-14) claims 1-3,12-15; examples 1-5 ---	1,2,5-16
A	SNOW A W ET AL: "FLUOROMETHYLENE CYANATE ESTER RESINS. SYNTHESIS, CHARACTERIZATION, AND FLUOROMETHYLENE CHAIN LENGTH EFFECTS" MACROMOLECULES, vol. 30, no. 3, 10 February 1997 (1997-02-10), pages 394-405, XP000678009 ISSN: 0024-9297 abstract ---	1,3
A	EP 0 581 268 A (KANEGAFUCHI CHEMICAL IND) 2 February 1994 (1994-02-02) claims 1,13 -----	1,4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 November 2000	16/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Glanddier, A

1

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5780159 A	14-07-1998	DE 4435992 A	11-04-1996
		WO 9611415 A	18-04-1996
		EP 0733221 A	25-09-1996
		JP 9507312 T	22-07-1997
EP 0581268 A	02-02-1994	DE 69315904 D	05-02-1998
		DE 69315904 T	27-08-1998
		JP 6122763 A	06-05-1994
		US 5360887 A	01-11-1994

PATENT COOPERATION TREATY

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REC'D 09 MAR 2001

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
PCFHG01		
International application No. PCT/EP00/06203	**International filing date** *(day/month/year)* 03/07/2000	**Priority date** *(day/month/year)* 01/07/1999
International Patent Classification (IPC) or national classification and IPC C08G73/06		
Applicant PIRELLI CAVI E SISTEMI S.p.A.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
16/01/2001	06.03.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Kairi, M Telephone No. +49 89 2399 8672

Form PCT/IPEA/409 (cover sheet) (January 1994)

I. Basis f the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:
   Description, pages:

   1-11 as originally filed

   Claims, No.:

   1-16 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   ☐ the language of publication of the international application (under Rule 48.3(b)).
   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.
   ☐ filed together with the international application in computer readable form.
   ☐ furnished subsequently to this Authority in written form.
   ☐ furnished subsequently to this Authority in computer readable form.
   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:
   ☐ the claims, Nos.:
   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-16
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-16
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

R It m V

R ason d statement under Articl 35(2) with r gard to n v lty, inv ntiv st p or industrial applicability; citations and explanations supporting such statement

Article 33(2) PCT

None of the prior art discloses an optical waveguide system or a structure or part thereof comprising a resin composed of at least one polycyanate copolymer obtainable by copolymerization of at least one difunctional organic cyanate with at least one fluorinated monocyanate.

Article 33(3) PCT

Closest prior art is considered to be the document US-A-5 780 159 (D1). D1 discloses an optical element comprising plastic, wherein said plastic is a polycyanurate resin derived from at least one polycyanate selected from the group disclosed in Claim 2 of D1. Said optical element is an optical device selected from the group consisting of waveguide structures, lenses, prisms, corrected lens systems, optical photoconductive fibers, substrates for optical coatings and adhesives for optical components (Claim 12).

The subject-matter of Claim 1 differs from D1 in that the polycyanate copolymer is obtainable by copolymerization of at least one difunctional organic cyanate with at least one fluorinated monocyanate.

The object of the present invention is to provide copolymers to be used in the preparation of optical waveguide systems or structures or parts thereof having low optical losses at 1.3 and at 1.55 µm.

The solution provided is non-obvious, since none of the prior art contains a hint as to the use of a copolymer obtainable by copolymerization of at least one difunctional organic cyanate with at least one fluorinated monocyanate for the preparation of an optical waveguide sytem or a structure or part thereof.

Re Item VII

Certain defects in the international application

The statement of prior art does not contain reference to the closest prior art US-A-5 780 159 (Rule 5.1(a)(ii) PCT).

Re Item VIII

Certain observations on the international application

1. Claims 5 and 13 refer to a brominated monocyanate of formulas I to III. However, formulas II and III correspond to dicyanates (Article 6 PCT).

2. The "about" associated with a range of an amount in Claims 7 and 15 and in the description provides uncertainty regarding the scope of protection of the present invention (Article 6 PCT).

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 January 2001 (11.01.2001)

PCT

(10) International Publication Number
WO 01/02464 A1

(51) International Patent Classification[7]: C08G 73/06, G02B 1/04

(21) International Application Number: PCT/EP00/06203

(22) International Filing Date: 3 July 2000 (03.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99112596.4 1 July 1999 (01.07.1999) EP

(71) Applicant *(for all designated States except US)*: **PIRELLI CAVI E SISTEMI S.P.A.** [IT/IT]; Viale Sarca, 222, I-20126 Milano (IT).

(72) Inventors; and
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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: WAVEGUIDE SYSTEMS OR STRUCTURES OR PARTS THEREOF, CONTAINING POLYCYANATE COPOLYMERS PREPARED FROM POLYFUNCTIONAL CYANATES AND FLUORINATED MONOCYANATES

(57) Abstract: The present invention is directed to wave guide systems or structures or parts thereof, characterized in that they consist of or comprise a resin composed of at least one polycyanate copolymer, obtainable by copolymerization of at least one specific difunctional cyanate with at least one monocyanate of the formula N≡C-O-R, wherein R is a straight or branched non-aromatic hydrocarbon radical or a non-aromatic hydrocarbon radical comprising a cyclic structure, the radical having the formula $C(R')_2$-CFR''_2 wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated alkyl or alkenyl group, and each of R'' may independently be defined as R' or may have an arylic structure. The at least one difunctional cyanate is selected from aromatic dicyanates having two arylic rings, connected with each other by a group Z wherein Z is a chemical bond, SO_2, CF_2 CH_2, CHF, $CH(CH_3)$, isopropylene, hexafluoroisopropylene, n- or iso-C_1-C_{10} alkylene, O, NR^9, N=N, CH=CH, C(O)O, CH=N, CH=N-N=CH, alkyl oxyalkylene having 1 to 8 carbon atoms, S, $Si(CH_3)_2$, and R^9 is hydrogen or C_1-C_{10} alkyl. The polycyanate copolymer may further comprise an aromatic monocyanate and/or one or more of brominated cyanates. The polycyanate copolymers are advantageously selected for the preparation of optical waveguide systems or structures or parts thereof because they have low optical losses at 1.3 and 1.55μm.

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Waveguide systems or structures or parts thereof, containing polycyanate copolymers prepared from polyfunctional cyanates and fluorinated monocyanates

The present invention is directed to optical elements in the field of waveguide systems or waveguide structures, e.g. arrayed wave guide components, prepared by copolymerization of specific polyfunctional cyanates and fluorinated monocyanates, as well as to the use of said copolymers for the preparation of said structures.

Organic polymers are increasingly interesting materials in the optical or microoptical field, in integrated optics or in microsystem techniques. In these fields, they may be used in optical instruments and apparatuses or parts thereof as well as in special optics as lenses, prisms, for fixation of optical systems, as support material for optical layers and as translucent coating materials for mirrors or lenses. Organic polymers may be used in optical fibres and for the preparation of waveguide structures. Their technical handling is relatively easy, and their density is lower in comparison to glass.

Specifically, if such plastics or organic polymers are to be used as a waveguide, a variety of requirements are to be met. The refractive index of the material should be variable in a range as broad as possible and should be adaptable to that of specific substrates. If used in the optical communication engineering, low absorptions of the materials are required at 1.3 and 1.55µm. The loss due to attenuation caused by volume defects (non-homogenities, microbubbles, microfissures) should be minimized. Besides specific technological requirements, e.g. preparation of layers and structurability, specific provisions for the use of organic polymers as waveguide structures in integrated optics are the thermal and thermo-mechanical stability, adapted extension coefficients and long term stability of optical properties.

Until now, polymethacrylates and polycarbonates have been mainly used for optical purposes. Both classes of polymers have an

excellent light transmittance, but their thermal and thermo-mechanical stability is not sufficient due to their chemical structure. Thus, polymethacrylates and polycarbonates cannot practically be used at temperatures exceeding 130°C which is due to their relatively low glass transition temperatures. In addition, both types of polymers are linear, un-crosslinked polymers. This has the adverse effect that they are partly solubilized in case multilayer-systems are prepared via the application of dissolved components, e.g. by spin-coating each layer. Consequently, the layer structures as obtained are not sufficiently delimitated and neat which, however, is an essential for the preparation of waveguide structures.

There are other high performance polymers which have glass transition temperatures of more than 180°C. Examples are polyarylethersulfones, polyarylsulfones, polyaryletherketones, polyimides and polyetherimides, the processing of which, however, is more difficult than that of polymethacrylates and polycarbonates. Another disadvantage of these systems is the relatively high optical loss at wave lengths of 1.3 and 1.55µm, relevant in communication engineering.

Polyperfluorocyclobutanes (PFCB) are a relatively new class of high performance polymers. Upon thermal curing they yield unsoluble cross-linked polymers which are characterized by high thermal stability. Waveguide layers prepared from PFCB show very low optical losses of 0.2 dB/cm at 1550 nm.

Also, polycyanurates have been used for the preparation of optical components. US patents 5 208 892 and 5 165 959 describe the preparation of polycyanate resins made of a single monomer (either fluorinated or non-fluorinated). German Offenlegungsschrift DE 44 35 992 A1 describes optical elements prepared from polycyanurate resins. The resins are made by polymerization of dicyanate or polycyanate compounds, optionally in mixture with di- or polyphenols or di- or polyglycidyl compounds. Like polyperfluorocyclobutanes, polycyanurates yield unsoluble cross-linked polymers upon thermal curing, and these

polymers are as well characterized by high thermal stability. They are specifically useful due to their excellent adhesional force on a variety of substrates, for example silicon, silica or a variety of organic polymers. Refractive index and glass transition temperature of the cured cross-linked polymers may be varied in broad ranges, due to the easy availability of a great number of di- and mono-functional cyanate monomers which may be copolymerized with each other. Polycyanurates of the kind mentioned above are partly commercially available. Completely cured polycyanurates known in the art which consequently are stable for long terms may have optical losses of about 0.2 dB/cm at 1.3µm. However, the optical losses are not less than 0.5dB/cm at 1.55µm which is important in communication engineering technologies.

The present invention provides copolymers, obtainable by copolymerization of at least one monocyanate, derived from a partly or fully fluorinated alcohol ("fluorinated monocyanate"), and at least one specific difunctional organic cyanate. It has been found that such copolymers are specifically valuable in the preparation of optical waveguide systems or structures thereof having low optical losses at 1.3 and at 1.55 µm.

Throughout the invention, "partly fluorinated" means that at least one fluorine atom is present in the molecule. "Fully fluorinated" means that hydrogen atoms are completely substituted by fluorine atoms. The whole molecules, or single organic radicals or groups (e.g. methyl, methylene, alkyl, aryl groups), respectively, may be fully fluorinated.

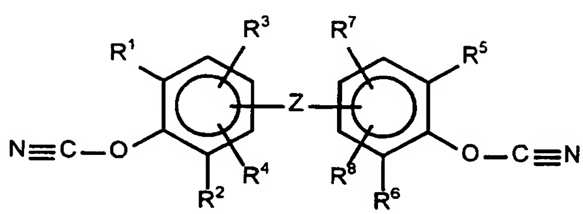
As fluorinated monocyanate, one, two, three or even more monocyanates of formula I may be used

$$N{\equiv}C{-}O{-}R \qquad (I)$$

wherein R is $C(R')_2{-}CFR''_2$, wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated alkyl or alkenyl group having preferably

1 to 13, more preferably 3 to 11 carbon atoms. Each of R" may independently be defined as R'. Further, R" may have an arylic structure. Preferably, R is a straight, branched, or cyclic non-aromatic hydrocarbon radical or an non-aromatic hydrocarbon radical comprising a cyclic structure. Preferably, the non-aromatic hydrocarbon radical has 1 to 15, more preferably 3 to 12 carbon atoms. It is to note that each of the carbon atoms of R may carry 1, 2 or, if it is a terminal carbon atom, 3 fluorine atoms. Fully fluorinated carbon atoms ($-CF_3$, $-CF_2-$) are preferred. Further, it is preferred that one or both of R' are hydrogen and/or one of R" is fluorine or a partly or fully fluorinated alkyl and the other is a partly or, more preferable, fully fluorinated alkyl which may be straight, branched or cyclic. Specific examples for the cyanates of formula (I) are $-CH_2-CF_2-CF_3$, $-CH_2-CF_2-CF_2-CF_3$, $-CH_2-C(CF_3)_2F$, $-CH_2-CF_2-CF_2-CF_3$.

For the preparation of the said copolymer, one, two, three or even more difunctional organic cyanates may be used. The expression "difunctional" means that two NCO groups are present in the molecule. The NCO groups are bound to organic radicals via the oxygen atom. The difunctional cyanate may be, but is not necessarily, partly or fully fluorinated. The organic structure of the difunctional cyanate or cyanates is selected under difunctional cyanates of formula II:



(II)

wherein R^1 to R^4 and R^5 to R^8 are independently from each other hydrogen, optionally substituted C_1-C_{10} alkyl, C_3-C_8-cycloalkyl, C_1-C_{10}-alkoxy, halogen, phenyl or phenoxy, the alkyl or aryl groups being unfluorinated, partly fluorinated or fully fluorinated, Z is a chemical bond, SO_2, CF_2 CH_2, CHF, $CH(CH_3)$, isopropylene, hexafluoroisopropylene, n- or iso-C_1-C_{10} alkylene

which may be partly or fully fluorinated, O, NR^9 with R^9 being hydrogen or C_1-C_{10} alkyl, N=N, CH=CH, C(O)O, CH=N, CH=N-N=CH, alkyloxyalkylene having 1 to 8 carbon atoms which is optionally partly or fully fluorinated, S, or $Si(CH_3)_2$. Examples are

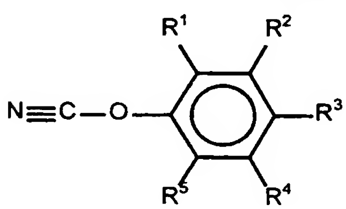
2,2'-bis(4-cyanato-phenyl)propane,
2,2'-bis(4-cyanato-phenyl)hexafluoropropane,
biphenylene-4,4'dicyanate,
2,3,5,6,2',3',5',6'octafluorobiphenylene-4,4'-dicyanate.

In one embodiment of the invention, dicyanates according to formula III:

$$N{\equiv}C{-}O{-}R^{10}{-}O{-}C{\equiv}N \qquad \text{(III)}$$

wherein R^{10} is an organic non-aromatic hydrocarbon group carrying at least 1 fluorine atom are copolymerized into the polycyanate copolymer useful in the present invention. In formula (III), R^{10} is preferably an alkylene group, more preferably having 3 to 12 carbon atoms. Each of the carbon atoms may carry 0, 1 or 2 or, in the case of a terminal group, 3 fluorine atoms. The carbon chain may be straight or branched or may be cyclic or may contain a cyclic part. Further, it may contain one or more C=C double bonds. In one embodiment, R^{10} is fully fluorinated. Examples are $-CH_2-CF_2-CF_2-CH_2-$ or $-CH_2-CF_2-CF_2-CF_2-CF_2-CH_2$.

In another embodyment of the present invention, at least one additional monocyanate having formula IV:



(IV)

wherein R^1 to R^5 are as previously defined for formula II, is copolymerized in addition to the starting cyanates as defined above (with or without (a) cyanate(s) of formula III) in order to obtain the polycyanate copolymer. Examples for compounds of formula IV are phenylcyanate and perfluorophenylcyanate.

Specifically, the refractive index and the glass transition temperature may be influenced by this additive as desired.

The polycyanate copolymers according to the invention may be obtained by mixing at least one of the monocyanates of formula I, optionally in addition to at least one of formula IV, and at least one difunctional organic cyanate of formula II, optionally in addition to at least one of formula III. The ratio of monocyanates to dicyanates may be freely chosen, provided that at least 1% by mol, preferably at least to 5% by mol, more preferably at least 10% by mol of monocyanate of structure I is present per mol of monomers to be polymerized. Preferably, the monofunctional cyanates of formulas I and IV are present in a molar amount of not more than 75% related to the total amount of moles of monomers present in the mixture to be copolymerized.

The starting monocyanate and dicyanate compounds as described above are preferably warmed up after mixing. The temperature may be chosen as required; a range of about 120°C to 170°C is preferred. Preferably, the reaction is performed in the absence of oxygen, e.g. in a sealed and preferably (under an inert gas atmosphere). The mixture is allowed to react until a liquid or viscous prepolymer (resin) is obtained. This prepolymer or resin is soluble in useful solvents, preferably in solvents having high polarity, e.g. ethylethoxyacetate or chlorobenzene. In general, the prepolymer is processed in a respective solution, e.g. by spin-coating of a solution containing 25 to 65% by weight of the prepolymer, more preferably about 50% by weight of the prepolymer. The prepolymer solution may be applied to a suitable substrate, consisting of e.g. silicon, quartz or an organic polymer. After being brought into the desired shape (e.g. a layer of desired thickness) it is cured (e.g. at temperatures in the range of 200° to 260°C) in order to provide the desired network between the cyanate groups.

If an optical wave guide system comprising a variety of different layers of the present polycyanate copolymers shall be

prepared, each different layer is applied and is cured, e.g. thermically cured, before the next layer is applied.

It shall be clear that the term "resin" is independent of the condition of the polymer, e.g. whether it is in a prepolymerized condition or is partly or completely cured.

The polycyanate copolymers according to the present invention have a glass transition temperature in the range of 100° to 300°C, and their refractive index at 1.55μm may be controlled in the desired range, specifically of from 1.35 to 1.60. Specifically, the more fluorinated monomers are used, or the more fluorine parts per weight are present in the mixture, related to the weight of the mixture to be polymerized, the lower is the refractive index of the polycyanate copolymer obtained.

On the other hand, use of brominated derivatives of the cyanate monomers as defined above will raise the refractive index of the copolymer obtained. Thus, monocyanate compounds of e.g. formula IV wherein at least one of R^1, R^2, R^3, R^4 o4 R^5 is substituted by bromine, may be advantageously added to the mixture. In general, the more bromine is included in the polymer, the higher is the refractive index obtained. Accordingly, any of the cyanates of formulas I to IV as defined above (with the proviso that those of formula I may be free of fluorine) carrying one or more bromine atoms may be selected. However, brominated monocyanates are preferably used, either alone or in mixture with brominated polycyanates.

The polycyanate copolymers according to the present invention are used for the preparation of optical wave guide systems or parts thereof. For example, they may be used for the preparation of waveguides and waveguide structures. For such structures, use of at least two different polycyanate copolymers is preferred, wherein a polycyanate copolymer having a lower refractive index may be used for buffer and/or cladding while a polycyanate copolymer differing from the first one and having a greater

refractive index may be used as the optical waveguide. At least one of these polycyanate copolymers should have been obtained according to the present invention. The selection will be easily made by a skilled person who is able to control the refractive index via the teachings given in this application. The layers show excellent adhesion to each other and to the substrate. Waveguide structures as described above may be prepared by known methods, e.g. RIE (Reactive Ion Etching).

The invention is now further illustrated by way of examples.

Example 1

12.9 g of a substituted dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is hexafluoroisopropyl) and 3.7 g of a partly fluorinated monocyanate (compound I wherein R is CH_2-CF_2-CF_2-CF_3) are heated to 160°C in a sealed vessel for a time of about four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 160°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of ethylethoxyacetate (EEA). Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4776 at 1.55 µm.

Example 2

12.9 g of a substituted dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is hexafluoroisopropyl), 3.7 g of a partly fluorinated monocyanate (compound I wherein R is CH_2-CF_2-CF_2-CF_3), and 1.3 g of a monocyanate (compound IV wherein R^1, R^2, R^4, R^5 are hydrogen and R^3 is bromine) are heated to 160°C in a sealed vessel for a time of about four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 160°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4870 at 1.55 µm.

Example 3

9.7 g of dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is isopropyl) and 2.5 g of a fully fluorinated monocyanate (compound I wherein R is C-$(CF_3)_2$) are heated to 140°C in a sealed vessel for a time of about four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 140°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.5596 at 1.55 µm.

Example 4

9.7 g of a substituted dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is hexafluoroisopropyl), 10.3 g of a partly fluorinated dicyanate (compound III wherein R^{10} is CH_2-CF_2-CF_2-CF_2-CF_2-CH_2) and 1.1 g of a partly fluorinated monocyanate (compound I wherein R is CH_2-CF_2-CF_2-CF_3) are heated to 140°C in a sealed vessel for a time of about four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 140°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which is cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.3689 at 1.55 µm.

Example 5

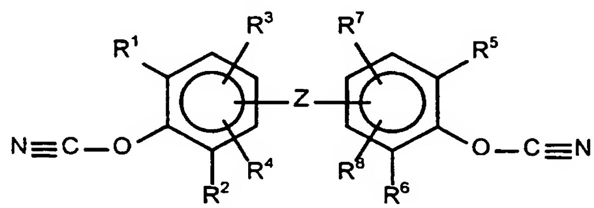
A 50 weight-% solution of the prepolymer of example 1 in EEA is spin-coated onto a silicon wafer, yielding a layer of about 8 µm thickness. Curing is performed at 240°C in a drying oven for one hour. Onto this layer, a 50 weight-% solution of the prepolymer of example 2 in EEA is spin-coated, again yielding a layer of about 8 µm thickness. Also, this layer is cured at 240°C in the drying oven for about 1 hour. According to known methods, an aluminum layer of about 100 nm is sputtered onto the said second prepolymer layer followed by its structurization by way of photolithography and chemical etching. Subsequently, the waveguides are structured by aid of oxygen RIE techniques (typical rate 100 nm/min using pure oxygen), and the etching mask is removed by treatment in a chemical etching bath. Then, the upper cladding layer is applied by spin-coating a prepolymer solution of example 1 followed by curing at 240°C for 1 hour. Using near field technique a difference of 0.0094 of the refractive index between the waveguide and its surrounding is measured. Cut-back measurements of light intensities of waveguides of different lenght yielded a loss of 0.35 dB/cm at 1.55 µm.

* * *

Claims:

1. Optical waveguide system or a structure or part thereof, comprising a resin composed of at least one polycyanate copolymer, obtainable by copolymerization of at least

one difunctional cyanate of formula II:



(II)

wherein R^1 to R^4 and R^5 to R^8 are independently from each other hydrogen, optionally substituted C_1-C_{10} alkyl, C_3-C_8-cycloalkyl, C_1-C_{10}-alkoxy, halogen, phenyl or phenoxy, the alkyl or aryl groups being unfluorinated, partly fluorinated or fully fluorinated, Z is a chemical bond, SO_2, CF_2 CH_2, CHF, $CH(CH_3)$, isopropylene, hexafluoroisopropylene, n- or iso-C_1-C_{10} alkylene, O, NR^9, N=N, CH=CH, C(O)O, CH=N, CH=N-N=CH, alkyl oxyalkylene having 1 to 8 carbon atoms, S, $Si(CH_3)_2$, and R^9 is hydrogen or C_1-C_{10} alkyl

with at least one monocyanate of the following formula I:

$$N{\equiv}C{-}O{-}R \qquad (I)$$

wherein R is a straight or branched non-aromatic hydrocarbon radical or a non-aromatic hydrocarbon radical comprising a cyclic structure, the radical having the formula $C(R')_2$-CFR''_2 wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated

alkyl or alkenyl group, and each of R" may independently be defined as R' or may have an arylic structure.

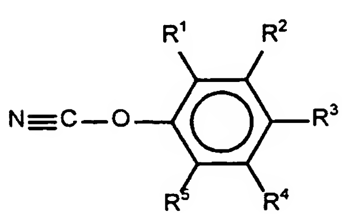
2. Optical waveguide system or a structure or part thereof according to claim 1, characterized in that the said polycyanate copolymer is obtainable by copolymerization of at least one difunctional cyanate of formula II, at least one monofunctional cyanat of formula I and at least one dicyanate having formula III:

$$N{\equiv}C-O-R^{10}-O-C{\equiv}N \qquad \text{(III)}$$

wherein R^{10} is a non-aromatic hydrocarbon group carrying at least one fluorine atom.

3. Optical waveguide system or a structure or part thereof according to claim 2, characterized in that R^{10} of formula III is a partly or fully fluorinated alkylene group having 1 to 15, more preferably 3 to 12 carbon atoms.

4. Optical waveguides system or a structure or part thereof according to any of the preceding claims, characterized in that the said polycyanate copolymer is obtainable by copolymerization of at least one difunctional cyanate of formula II, at least one monofunctional cyanate of formula I, optionally at least one dicyanate having formula III, and a monocyanate of formula IV



(IV)

wherein R^1 to R^5 are defined as in formula II.

5. Optical waveguide system or a structure or part thereof according to any of the preceding claims, characterized in that the said polycyanate copolymer is obtainable by copolymerization of at least one difunctional cyanate of formula II, at least one monofunctional cyanat of formula I, and at least one brominated monocyanate of formulas I to III, preferably of formula I, as defined above with the proviso that the monocyanates of formula I may be free of fluorine.

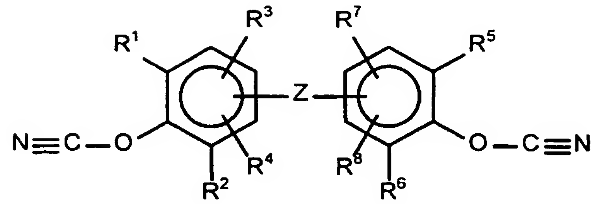
6. Optical waveguide system or a structure or part thereof according to any of the preceding claims, characterized in that the monocyanate of formula I as defined in claim 1 is used in an amount of at least 10%, preferably of at least 20% by mol per mol of the polycyanate copolymer.

7. Optical waveguide or a structure or part thereof according to any of the preceding claims, characterized in that the polycyanate copolymer has a glass transition temperature of from 100°C to 300°C and/or has a refractive index of about 1.35 to about 1.60 at 1.55μm.

8. Optical waveguide system or a structure or part thereof according to any of the preceding claims, characterized in that it is an optical fibre, a waveguide, a buffer layer, a cladding or a support for any of the said structures.

9. Optical waveguide system comprising a waveguide consisting of a resin composed as defined in any of claims 1 to 7, and a buffer and/or cladding consisting of a resin composed of a resin as defined in any of claims 1 to 7, but different from that of the waveguide, wherein the resin of the waveguide has a greater refractive index than that of the buffer and/or cladding.

10. Use of a polycyanate copolymer, obtainable by copolymerization of at least one polyfunctional cyanate selected from a difunctional cyanate of formula II:



(II)

wherein R^1 to R^4 and R^5 to R^8 are independently from each other hydrogen, optionally substituted C_1-C_{10} alkyl, C_3-C_8-cycloalkyl, C_1-C_{10}-alkoxy, halogen, phenyl or phenoxy, the alkyl or aryl groups being unfluorinated, partly fluorinated or fully fluorinated, Z is a chemical bond, SO_2, CF_2 CH_2, CHF, $CH(CH_3)$, isopropylene, hexafluoroisopropylene, n- or iso-C_1-C_{10} alkylene, O, NR^9, N=N, CH=CH, C(O)O, CH=N, CH=N-N=CH, alkyl oxyalkylene having 1 to 8 carbon atoms, S, $Si(CH_3)_2$, and R^9 is hydrogen or C_1-C_{10} alkyl

with at least one monocyanate of the following formula I:

N≡C-O-R (I)

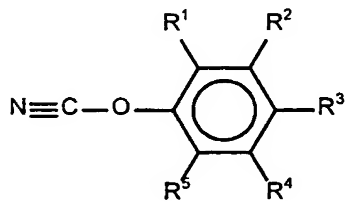
wherein R is a straight or branched non-aromatic hydrocarbon radical or a non-aromatic hydrocarbon radical comprising a cyclic structure, the radical having the formula $C(R')_2$-CFR''_2 wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated alkyl or alkenyl group, and each of R" may independently be defined as R' or may have an arylic structure, as a material in optical waveguide systems or structures or parts thereof, preferably of optical fibres, waveguides, buffers, claddings, or supports for such structures.

11. Use of a polycyanate copolymer according to claim 10, characterized in that the said polycyanate copolymer is obtainable by copolymerization of at least one difunctional cyanate of formula II, at least one monofunctional cyanat of formula I and at least one dicyanate having formula III:

$$N{\equiv}C\text{-}O\text{-}R^{10}\text{-}O\text{-}C{\equiv}N \qquad \text{(III)}$$

wherein R^{10} is a non-aromatic hydrocarbon group carrying at least one fluorine atom, preferably a partly or fully fluorinated alkylene group having 1 to 15, more preferably 3 to 12 carbon atoms.

12. Use of a polycyanate copolymer according to claim 10 or 11, characterized in that the said polycyanate copolymer is obtainable by copolymerization of at least one difunctional cyanate of formula II, at least one monofunctional cyanate of formula I, optionally at least one dicyanate having formula III, and a monocyanate of formula IV



(IV)

wherein R^1 to R^5 are defined as in formula II.

13. Use of a polycyanate copolymer according to any of claims 10 to 12 10, characterized in that the said polycyanate copolymer is obtainable by copolymerization of at least one difunctional cyanate of formula II, at least one monofunctional cyanat of formula I, and at least one brominated monocyanate of formulas I to III, preferably of formula I, as defined above with the proviso that the monocyanates of formula I may be free of fluorine.

14. Use of a polycyanate copolymer according to any of claims 10 to 13, characterized in that the monocyanate of formula I as defined in claim 1 is used in an amount of at least 10%, preferably of at least 20% by mol per mol of the polycyanate copolymer.

15. Use of a polycyanate copolymer according to any of claims 10 to 14, characterized in that the said polycyanate copolymer has a glass transition temperature of from 100°C to 300°C and/or has a refractive index of about 1.35 to about 1.60 at 1.55µm.

16. Use of a polycyanate copolymer according to any of claims 10 to 15, wherein at least the materials used for the optical waveguide and for the buffer/and or cladding are those as defined in claim 10 and the material for the waveguide has a grater refractive index than that of the buffer and/or cladding.

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INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/EP 00/06203

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G73/06 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 780 159 A (BAUER MONIKA ET AL) 14 July 1998 (1998-07-14) claims 1-3,12-15; examples 1-5	1,2,5-16
A	SNOW A W ET AL: "FLUOROMETHYLENE CYANATE ESTER RESINS. SYNTHESIS, CHARACTERIZATION, AND FLUOROMETHYLENE CHAIN LENGTH EFFECTS" MACROMOLECULES, vol. 30, no. 3, 10 February 1997 (1997-02-10), pages 394-405, XP000678009 ISSN: 0024-9297 abstract	1,3
A	EP 0 581 268 A (KANEGAFUCHI CHEMICAL IND) 2 February 1994 (1994-02-02) claims 1,13	1,4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 November 2000	16/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Glanddier, A

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. al Application No
PCT/EP 00/06203

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